
New Vibrational Self-Consistent Field Program for Large Molecules

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ABSTRACT

A recently developed, general computer program that performs vibrational self-consistent field (VSCF) calculations for large molecules is described. The program, which we refer to as VSCF_95, requires as its only input a force field in mass-scaled normal coordinates. Currently, it is limited to a maximum of 200 normal modes, and the force field is limited to coupling terms involving a maximum of six normal modes, with a maximum order of six in any normal mode. As output the program returns VSCF energies for specified quantum states. We illustrate the code with two new applications. The first is to HCO, for which we use a full sixth-order force field. The second is to a model of the fullerene, C₆₀, for which we have calculated a 75,731-term force field, which includes all anharmonic terms up to fifth order, and all two-mode coupling terms up to fourth order. © 1996 by John Wiley & Sons, Inc.

Introduction

Vibrational self-consistent field (VSCF) calculations have been performed on small molecules for more than a decade.^{1,2} In 1985, Romanowski and Bowman developed the program POLYMODE,³ which performs VSCF calculations for molecules as large as pentaatomics. That code also does configuration mixing calculations. POL-

YMODE requires, as input, a force field, which is limited to terms up to fourth order, in mass-scaled normal coordinates.

An important application of POLYMODE was a calculation of many vibrational eigenstates of formaldehyde, H₂CO.⁴ In that application, both VSCF and converged, configuration mixing calculations were done. It was found that the converged results differed from the simple, normal-mode, harmonic results by between 28 and 150 cm⁻¹ for the fundamentals, illustrating the necessity of improvement beyond the simple, harmonic approximation. By contrast, the VSCF results differed from the converged ones by between 3 and 33 cm⁻¹ for the fundamentals. In the formaldehyde calculation, a complete fit was performed of the potential energy

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surface to fourth order in mass-scaled normal coordinates.

As noted above, POLYMODE is limited to quartic force fields for at most nine modes. The necessity for a computer code that will generate VSCF energies for larger molecules is apparent. Very recently, a study of the vibrational motions of bovine pancreatic trypsin inhibitor protein appeared.⁵ This molecule has 3435 vibrational degrees of freedom, of which the 88 lowest frequency ones were considered in a VSCF calculation, which employed a limited quartic force field. This calculation showed clearly that the horizon for vibrational treatment of systems larger than pentaatomics is in sight. Thus, we have developed a new code to do VSCF calculations, and we report the features of this code, and two new applications to HCO and a model for C_{60} in this article.

The new code we have written will accept an arbitrarily large number of modes, limited only by the size of the computer memory. (The present version is configured for 200 modes.) It is very fast and much more flexible than POLYMODE. Briefly, the VSCF program, which we call "VSCF_95," reads a force field in mass-scaled, normal-mode coordinates, and returns the VSCF energies for specified quantum-state configurations. This code will be made available for public use through the Quantum Chemistry Program Exchange, or by contacting one of us (J. M. Bowman). The VSCF program has been tested on formaldehyde, and the results in Ref. 4 were reproduced. The results of a new application to HCO, which is very anharmonic, and a preliminary study of the fullerene, C_{60} , are reported here. Also presented are the methods we used to calculate the force constants needed to assemble the force fields for the VSCF program.

Vibrational SCF Theory

We present here a brief review of the VSCF theory as used by the new program. For a more general introduction to the VSCF approach see Ref. 1. The relevant Hamiltonian for a nonrotating, N -mode molecule is given in mass-scaled normal coordinates as follows⁷:

$$\hat{H} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2} \frac{d^2}{dQ_i^2} + \frac{1}{2} \omega_i^2 Q_i^2 \right) + V_{ac}(Q_1, Q_2, \dots, Q_N) \quad (1)$$

where ω_i is the harmonic frequency of mode i , and V_{ac} contains the anharmonic and coupling terms. It is represented as a multinomial,

$$V_{ac}(Q_1, Q_2, \dots, Q_N) = \sum_{i,j,k} f_{ijk} Q_i Q_j Q_k + \sum_{i,j,k,l} f_{ijkl} Q_i Q_j Q_k Q_l + \dots \quad (2)$$

where the subscripts ijk , etc., run over all modes with, at this point, no restrictions. Coupling terms obviously involve coordinates of different modes, and anharmonic terms involve coordinates of a single mode. We denote the uncoupled anharmonic oscillator terms as UAO terms.

The VSCF wave function is written as a simple Hartree-product of single-mode wave functions. The variationally optimized form of such a wave function leads to N -coupled, integrodifferential eigenvalue equations. These are solved via an iterative procedure to self-consistency. In general, the eigenvalue equation to be solved for mode i is of the form:

$$(\hat{h}_i^{vscf} - \varepsilon_{n_i}^{(i)}) \chi_{n_i}^{(i)}(Q_i) = 0, \quad (3)$$

where:

$$\hat{h}_i^{vscf} = \hat{h}_i^0 + \sum_{p=1} c_i^{(p)} Q_i^p, \quad (4)$$

and where \hat{h}_i^0 is the harmonic-oscillator Hamiltonian for mode i . The $c_i^{(p)}$ are constants that arise from UAO terms in the force field, and also from averaging terms involving modes j , not equal to i , over the wave functions for those modes.

Each of the single-mode wave functions, $\chi_{n_i}^{(i)}(Q_i)$, is expanded in a basis of harmonic-oscillator functions, which are eigenfunctions of \hat{h}_i^0 . This choice of basis functions leads to analytical expressions for all the potential matrix elements.⁶

The total energy after convergence is not equal to the sum of the SCF eigenvalues, since the sum of single-mode Hamiltonians, \hat{h}_i^{vscf} , is not equal to the full Hamiltonian. The reason for this is overcounting. Consider the form for V_{ac} above. The energy corresponding to the term $f_{ijk} Q_i Q_j Q_k$ appears in the three Hamiltonians, \hat{h}_i^{vscf} , \hat{h}_j^{vscf} , and \hat{h}_k^{vscf} . Thus, in calculating the expectation value of the total Hamiltonian we have to subtract two times the expectation value of this potential term.

Description of Computer Program

The VSCF program is based on the theory presented in the previous section. The purpose of this program is to perform VSCF calculations on arbitrarily large systems. The program requires as its only input a force field of the molecule in an expanded, normal coordinate form.

The program reads the force field from an input file, and the harmonic normal-mode energies are calculated from the harmonic force constants. The size of the harmonic basis set to use in the calculation is specified in the header of the input field containing the force field. The quantum states for which output is desired are specified in the footer of the input file. A subroutine is called which calculates the harmonic basis set integrals $\langle i|Q^n|j\rangle$ for $n = 1, \dots, 6$, and where $|i\rangle$ and $|j\rangle$ refer to harmonic-oscillator functions. The outermost loop performs the VSCF calculation for each quantum state specified in the footer. The VSCF loop begins, and the Hamiltonians \hat{H}_i^{vscf} are formed and the eigenvalue equations [eq. (3)], are solved. As the iteration process continues, the VSCF Hamiltonians are updated by averaging V_{ac} over the single-mode eigenfunction of the previous diagonalizations. Overcounting terms are subtracted from the sum of the VSCF eigenvalues to obtain the VSCF energy. Convergence is achieved when the VSCF energy does not change to within a specified tolerance.

To use the program, a single input file containing the force field, a header, and a footer, is required. The header contains four integers and might look like:

```
174 10 75731 175
```

The first integer specifies the number of vibrational modes in the molecule, which for C_{60} is 174. The second integer specifies the size of the primitive harmonic basis set that will be used in the calculation. In this example, ten functions are used. The third integer specifies the number of force constants, and thus the number of terms in the force field. The final integer specifies the number of states to be calculated, which is 175 in the above example. In the present code, the maximum number of coupled modes is six, and this determines the format of the input for the force field, which consists of lines containing twelve integers and a

double-precision real number. An example of one such line is:

```
17 40 0 0 0 0 1 3 0 0 0 0 .1138908D-18
```

This line represents the two-mode coupling term, $f_{17,40,40,40} Q_{17} Q_{40}^3$, with $f_{17,40,40,40} = 0.1138908 \times 10^{-18}$. The first six integers specify a group of six normal modes. If only one mode number is listed, the line represents a harmonic or anharmonic term; if more than one mode number is listed, the listed modes are coupled in the force-field term. The first zero in the first six integers, from left to right, marks the end of the mode numbers, and thus no zeros may be placed between mode numbers. The next six integers specify the power to which each specified mode is raised in the force-field term. The final real number is the corresponding force constant in mass-weighted atomic units. The order of these lines is arbitrary, except that the harmonic terms (in any order) must precede all other terms.

The first line of the footer consists of one integer that specifies the default quantum state for all modes. Subsequent lines consist of two integers, the first specifies a single mode quantum state and the second specifies the mode that should be raised to that state while all other modes remain at the default state. For the above example, but for three states instead of 175, the footer might be:

```
0
1 1
1 2.
```

The program would calculate the energy for all modes in the ground state, the energy for mode 1 in the quantum state 1, and all other modes in the ground state, and the energy for mode 2 in the quantum state 1, and all other modes in the ground state. If the first integer, 0 in the above example, is any negative number, then the program expects a list of quantum numbers for each mode for the number of states specified in the header.

As stated above, and as evident from the VSCF program input file, the program can accommodate coupling between as many as six modes. Each mode is limited to sixth order, and thus anharmonic terms are limited to sixth order, but a coupling term consisting of six modes may have an overall order as high as 36. Increasing beyond a sixth-order calculation requires changes to the code, but no change in the logic of the program. (POLYMODE is limited to fourth-order force fields, i.e., coupling among a maximum of four modes, and also a total multinomial order of a maximum of 4.)

The new VSCF program is also designed to accommodate arbitrarily large systems. Three parameters define the size of the calculation, and are listed in a parameter statement at the beginning of the program. The first parameter is *nmax*, the maximum size of the harmonic basis set that can be used in the calculation. *Nmax* is currently set to 50. All of our calculations have used a harmonic basis set of 10 or 20. The second parameter is *maxmodes*, the largest number of modes the program can accommodate. *Maxmodes* is currently set to 200. The third parameter is *mult*, the number of force constants, per mode, that can be used in the calculation. Currently, *mult* is set to 400, and thus the program can accommodate $400 \times 200 = 80,000$ force constants. These parameters can easily be adjusted by the user.

Two applications of the code are presented next. The first is to a small radical, HCO, for which an accurate *ab initio* potential is available. The second is to a model of C_{60} .

Application to HCO

We fit the *ab initio* global potential of $HCO^{8,9}$ to a full sixth-order force field in mass-scaled normal coordinates. The force field was determined by a standard least-squares fit to a grid of 9261 potential values obtained from the potential energy surface. The grid was equally spaced in each normal coordinate, with 21 points per coordinate. The range for each coordinate spanned the classical turning points of the first excited harmonic energy. (Details are given below in the section describing the C_{60} calculations.) Table I contains the corresponding input for VSCF_95 (the numbers in Table I contain excess digits, well beyond the accuracy of the fit), and Table II contains the energies of the fundamentals and the zero-point energy, along with exact results from an earlier calculation,¹⁰ and harmonic results. As seen, the VSCF results are a substantial improvement over the harmonic ones, and in very good agreement with the exact ones.

We also did VSCF calculations using a full fourth-order force field (which is the type of force field used in POLYMODE). The results are far less accurate than those for the sixth-order force field. This may not be a general result, because HCO is a highly anharmonic, coupled molecule, even at low

levels of excitation. Both anharmonic and inter-mode coupling terms in the force field are significant, as a perusal of Table I will reveal.

Application to C_{60}

C_{60} is a large molecule of considerable current interest and thus is a good test case for this program. An empirical potential energy surface is used in our calculations. From this surface we calculated the force field to be used by the VSCF program. The VSCF program was then run with the force field as input. Presented here are the descriptions of the potential function used, the methods by which the force field was constructed, the composition of the force field used in the VSCF calculations, and the results from the VSCF calculations.

FORCE-CONSTANT MODEL

The structure of the C_{60} molecule is such that it contains 12 pentagons and 20 hexagons of carbon atoms in a soccer-ball-shaped arrangement with icosahedral symmetry. There are two types of bonds between atoms: a mostly single bond of equilibrium length 1.46 Å that exists between atoms on the same pentagon and a mostly double bond of equilibrium length 1.40 Å that exists between atoms on the same hexagon, but not on the same pentagon. Due to the remarkable symmetry of C_{60} , every atom is the same in that it has three nearest neighbors, two at an equilibrium distance of 1.46 Å, and one at an equilibrium distance of 1.40 Å. Each atom has six second-nearest neighbors.

The potential we use is based on the empirical Jishi et al.¹¹ model, and is very fast to evaluate. This potential model contains two types of terms: those that involve two-atom stretches and those that involve three-atom bends. The form of a stretch term between two atoms *i* and *j* is given by

$$V_s^{ij} = \frac{1}{2}s(r - r_e)_{ij}^2 \quad (5)$$

where *s* represents one of four force constants, depending on the nature of the *ij*-pair, *r* is the distance between atoms *i* and *j*, and *r_e* is the equilibrium distance between atoms *i* and *j*. Of the four force constants, symbolized collectively by *s*, *s_p* represent the stretch between two nearest

TABLE I.
Sample Input for VSCF_95 Program for HCO.

3 10 79 4			
100000200000	.134756592737557D - 04	300000600000	.115940933157861D - 09
200000200000	.371358360559059D - 04	100000300000	-.770094513765797D - 08
300000200000	.831444686756287D - 04	130000210000	.480483088265505D - 06
120000210000	.882241284910148D - 09	123000111000	-.347506606323834D - 06
120000120000	.167251769566050D - 07	200000300000	-.385137330785915D - 06
130000120000	.128951260100281D - 07	230000120000	.149815629832150D - 06
230000210000	.140997605476234D - 06	100000400000	.151337978730239D - 08
300000300000	-.266422077979072D - 05	130000310000	.790344510872853D - 08
120000310000	.203823737623801D - 09	123000211000	.382855169652524D - 08
120000220000	.228639483679358D - 08	120000130000	.464804738728460D - 09
130000220000	-.530593106969220D - 07	123000112000	.128797390180031D - 07
123000121000	.212947140896142D - 08	200000400000	.192367820149172D - 08
130000130000	-.352680548879017D - 07	230000220000	-.757396722955966D - 08
230000310000	.556230710619539D - 08	300000400000	-.122068140505185D - 07
230000130000	-.233852249214872D - 07	120000410000	.102750587445098D - 10
100000500000	.193502322403120D - 10	120000320000	.213570331617425D - 10
130000410000	-.218147589188611D - 09	130000320000	-.199210712076186D - 09
123000311000	.271554104313450D - 09	123000221000	.317166360885493D - 10
120000230000	.381395976673183D - 10	130000230000	.118155107209582D - 08
123000212000	-.870427388711004D - 10	123000131000	.141186556010989D - 09
120000140000	-.138808248796072D - 10	123000113000	-.509624749596595D - 09
123000122000	-.556663796613990D - 09	200000500000	-.115375323713863D - 10
130000140000	.971928319335557D - 09	230000320000	-.247111696559281D - 09
230000410000	.418545983935839D - 10	230000140000	-.100974154616262D - 09
230000230000	-.265854979745189D - 09	100000600000	-.142717136096625D - 11
300000500000	.739641755061357D - 09	130000510000	-.561934357046309D - 11
120000510000	.202953865791601D - 12	123000411000	.121437021951961D - 11
120000420000	-.869568878864600D - 12	120000330000	.176133123162491D - 11
130000420000	.958655057322147D - 11	123000312000	-.171161671580713D - 10
123000321000	.133851161406854D - 11	120000240000	-.174416005885788D - 12
130000330000	-.140265044365634D - 11	123000222000	-.132710719511417D - 10
123000231000	.673160389648037D - 11	130000240000	.262869904890532D - 10
123000213000	-.136921769973994D - 10	123000141000	.446493061314820D - 11
120000150000	.258237439009282D - 11	123000123000	-.132480081605793D - 10
123000132000	-.136228522724427D - 10	130000150000	.116071596779533D - 09
123000114000	.319603345948890D - 10	230000510000	-.812825568338442D - 11
200000600000	.476303087922078D - 11	230000330000	-.111859805662160D - 10
230000420000	-.388993957713762D - 11	230000150000	.102923221428083D - 09
230000240000	.105086961447926D - 10	0	
		11	
		21	
		31	

neighbor atoms on the same pentagon and s_h represents the stretch between two nearest neighbor atoms on the same hexagon, but not the same pentagon. The force constant s_2 describes the stretch between an atom and one of its second-nearest neighbors, and the force constant s_3 describes the stretch between an atom and one of its third nearest neighbors, that is, the one directly across the hexagon from a given atom.

The form of a bend term between three atoms i , j , and k or, more precisely, between two vectors ij and ik is given by:

$$V_b^{ijk} = \frac{1}{2}b(\theta - \theta_e)_{ijk}^2 \quad (6)$$

where b represents one of four possible force constants, θ is the angle between the vectors ij and ik , and θ_e is the equilibrium value of the angle be-

TABLE II.
Comparison of Harmonic, VSCF, and Exact Vibrational Zero-Point (ZPE) and Fundamental Energies (per Centimeter) for HCO.

	Harmonic	VSCF	Exact ^a
ZPE	2895.5	2843.5	2840.4
ν_1	1157.5	1108.5	1104.2
ν_2	1892.0	1888.1	1885.4
ν_3	2741.4	2443.9	2449.7

^a From Ref. 10.

tween the two vectors ij and ik . Of the four force constants symbolized by b , b_p represents the bend of a pentagon angle and b_h represents the bend of a hexagon angle. The force constant b_2 represents the bend of an angle formed by two vectors, one that extends from an atom to one of its nearest neighbors and another that extends from the atom to one of its second-nearest neighbors. Similarly, the force constant b_3 represents the bend of an angle formed by two vectors, one that extends from an atom to one of its nearest neighbors and another that extends from the atom to one of its third-nearest neighbors. The values of the eight force constants are presented in Table III.

With no further modifications, the total potential, V , is given by:

$$V = \frac{1}{2} \sum_{n=1}^4 \left(\sum_{ij} s_n (r - r_e)_{ij}^2 + \sum_{ijk} b_n (\theta - \theta_e)_{ijk}^2 \right) \quad (7)$$

For our calculations, we made a simple modification to this potential to introduce anharmonicity. This was done by the introduction of Simons-Parr-Finlan (SPF) coordinates¹² to the nearest-neighbor stretch terms. As a result, our potential energy function is no longer harmonic. (Previously, Weeks¹³ considered an anharmonic model of C_{60} in classical trajectory calculations of the power spectrum.) As a result of our modification, the term $\frac{1}{2} s_I (r - r_e)^2$, where $I = \{p, h\}$, becomes $\frac{1}{2} s_I r_e^2 (r - r_e/r)^2$. This substitution introduces an-

TABLE III.
Values of Eight Force Constants for C_{60} Potential.

s_p	2.35 ^a	b_p	1.00 ^b
s_h	4.00	b_h	0.250
s_2	1.21	b_2	0.095
s_3	-1.05	b_3	0.325

^a Units are in millidynes per angstrom.^b Units are in millidynes per sq. radian.

harmonicity without changing the normal-mode frequencies. We denote this as the SPF-modified potential.

FORCE FIELD

For the SPF-modified potential described above, a force field was created. First, a standard normal-mode analysis was performed, and the harmonic energy of each of the 174 vibrational normal modes was calculated. From these energies, the harmonic force constants were calculated. Next the UAO force constants were calculated. A one-dimensional grid along each of the normal coordinates was created, and the potential was evaluated at evenly spaced points along the grid. The harmonic term was subtracted in each case, and the values were fit using a least squares routine to the fifth-order form:

$$V_{ac}(Q_i, 0, \dots, 0) = f_{iii} Q_i^3 + f_{iiii} Q_i^4 + f_{iiiii} Q_i^5 \quad (8)$$

for normal mode i . Experiments were performed concerning both the number of grid points and the physical extent of the grid. The extent of the grid in each of the normal-mode coordinates, Q_i , was based on the value of the classical turning points for a given eigenstate, $|n\rangle$, of the harmonic Hamiltonian. These points are given by:

$$Q_i^\pm = \pm \sqrt{\frac{2}{f_{ii}} \left(n + \frac{1}{2} \right)} \quad (9)$$

Using this equation, Q_i^\pm were calculated and used as the endpoints of the grid, and sample points were then evenly spaced along the grid. The calculations we performed used both $n = 0$ and $n = 1$; the resulting differences in the force fields were very slight. For the calculation of the above UAO terms a 1-d grid with 21 points was used. In general (ignoring symmetry), for each of the 174 modes there are three UAO terms to consider and thus $3 \times 174 = 522$ terms in all. However, from the fit a large number of terms are zero, due to symmetry, and thus the final number of UAO terms equaled 302. All calculations were performed using a 14-node IBM SP2 computer, and this calculation required approximately 1.25 minutes of computer time.

The calculation of coupling force constants is a difficult task for large systems. Here we considered coupling only between two modes at a time. Such a model is far from accurate but will offer a

glimpse at the contribution coupling makes in defining the vibrational configuration of C_{60} . The calculation of coupling force constants is based on an extension of the grid calculation to two dimensions. A grid along two normal modes, with all other mode coordinates set to zero, was specified by the number of grid points and by the physical extent of the grid in each dimension as in the UAO case. The potential was calculated at each grid point, with harmonic and UAO terms subtracted, and a least-squares fit was performed. Only terms which have a combined order of ≤ 4 were considered. The potential data were fit to an equation of the form:

$$\begin{aligned} V_{ac}(Q_i, Q_j, 0, \dots, 0) \\ = f_{iij}Q_i^2Q_j + f_{ijj}Q_iQ_j^2 + f_{iii}Q_i^3Q_j \\ + f_{iiij}Q_i^2Q_j^2 + f_{ijjj}Q_iQ_j^3 \end{aligned} \quad (10)$$

for two modes, i and j , under consideration. Considering only two-mode coupling, to fourth order, between all modes, there are already $5 \times (173 + 172 + \dots + 1) = 75,255$ coupling terms to be considered. Some of the terms are zero, due to symmetry; however, we decided to retain all terms to provide a general test of the program. The calculation of the two-mode force field was done with an 11×11 grid with $n = 0$ and required approximately 40 minutes of computer time. Adding these two-mode terms to the harmonic and anharmonic ones obtains the final force field, which contains 75,731 terms. This force field is available upon request to J. M. Bowman.

VSCF CALCULATION

After the coupling force constant calculations were completed, the force field was run through the VSCF program. Calculations were performed using harmonic basis sets containing 10 and 20 functions; the results for both calculations were the same. The energy of the configuration in which all normal modes were in the ground state was calculated, and then a calculation was performed for each mode in its first excited state while every other mode remained in the ground state. To calculate the UAO energies, a force field containing only harmonic and UAO terms was used as input to the program. The calculations using the full force field required approximately 16 hours of CPU time if 20 basis functions were used and 4.5 hours if 10 basis functions were used. The calculations

using a force field consisting only of harmonic and UAO terms required approximately 2.5 minutes if 20 harmonic basis functions were used and 30 seconds if 10 basis functions were used.

Figure 1 is a plot of the UAO and VSCF energy differences relative to the normal-mode harmonic energies. Due to the high symmetry of C_{60} , there are only 46 distinct vibrational frequencies. Thus, the plots in Figure 1 are given as a function of the frequency group. As seen, the UAO differences are rather small; however, the VSCF energies are significantly different from the harmonic ones. This indicates, in a qualitative way, at least, that normal-mode coupling is significant in C_{60} .

Conclusions

We reported the development of a code which does vibrational SCF calculations quickly and flexibly for many-mode systems. The code has been tested on previously calculated systems, such as formaldehyde, and in a new calculation for HCO. In addition, a preliminary calculation of the vibrational structure of C_{60} was reported. A major component of the calculation is the assumed existence of a normal-coordinate force field, which can be up to sixth order in a single coordinate, and which can contain coupling terms among a maximum of six coordinates. Such force fields are relatively easy to obtain for small molecules; however, they can be fairly computer-intensive to obtain for large molecules, such as C_{60} . Efficient strategies to ob-

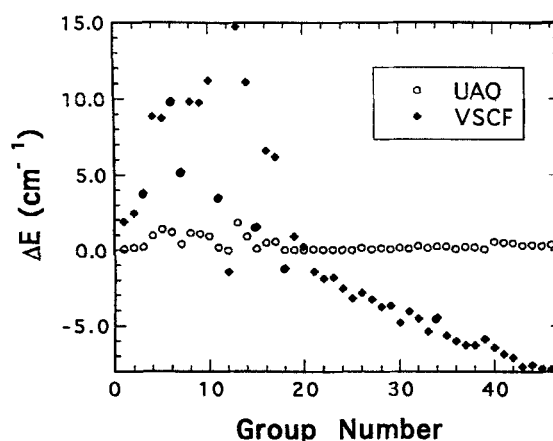


FIGURE 1. Energy differences (per centimeter) for UAO and VSCF calculations relative to the harmonic group number for C_{60} .

tain realistic force-fields for large molecules remains an area for research. Given the force field, the VSCF calculation itself is quite fast, and should prove useful in applications which require a realistic vibrational spectrum.

Finally, we note that a number of extensions of the code are possible and desirable. As already noted, the restriction to a maximum of 200 modes can easily be relaxed. The addition of terms in the Hamiltonian to describe rotation as well as Coriolis coupling is straightforward. It is also possible to go beyond the VSCF level of treatment by doing limited configuration mixing, as is done in POLYMODE. We plan to explore adding all of these extensions in the future.

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